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14. ABSTRACT
This project was aimed at elucidating the electronic structure of nitride semiconductor surfaces, defects, and impurities through first-principles calculations. Density functional theory is the standard approach, but in its routine implementation it has major deficiencies because the band gap of semiconductors is severely underestimated. A new approach based on "hybrid functionals" was used to overcome this problem. Two main topics were pursued. (1) Behavior of fluorine in nitride semiconductors. A thorough understanding of the behavior of interstitial fluorine was developed. It was proposed that fluorine acceptors may be useful for p-type doping of wide-band-gap semiconductors. (2) Effects of surfaces on the two-dimensional electron gas (2DEG) in high electron mobility transistors (HEMTs). It was determined that oxidized surfaces, which represent the realistic condition of the surface, are most relevant. To investigate surface oxidation, detailed calculations were performed for all possible structures that can occur with up to two monolayers of oxygen coverage, on both polar and nonpolar surfaces. The corresponding electronic structure produces information about surface states and Fermi-level pinning. In combination with Schroedinger-Poisson simulations, this enabled a

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Abstract continued

thorough understanding of how the surfaces affect the 2DEG. The results have been compared with experiments, leading to several joint theoretical/experimental publications.

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First-principles investigations of defects and surfaces and their impact on nitride devices

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Final Report

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1. Methodology

This project was aimed at elucidating the electronic structure of nitride semiconductor surfaces, defects, and impurities through first-principles calculations. Density functional theory is the standard approach, but in its routine implementation it has major deficiencies because the band gap of semiconductors is severely underestimated. Very recently, a new approach using "hybrid functionals" has emerged. Through a collaboration with Prof. Georg Kresse at the University of Vienna, the main developer of the VASP code, we obtained access to a code that could perform such calculations. This approach has been used extensively throughout this project, putting us at the forefront of applying this new methodology to problems relating to surface and defect states.

2. Effects of fluorine on nitride materials and devices

Fluorine has a beneficial effect on the characteristics of AlGaN/GaN high electron mobility transistors (HEMTs), but the causes are not understood. We conducted investigations of fluorine in interstitial and substitutional sites, and its interaction with point defects. These studies produced the really intriguing result that fluorine placed at interstitial sites in GaN or AlN acts as a shallow acceptor. For a material that is hard to dope *p*-type, such as AlN (and the same applies to ZnO), such an approach might overcome the obstacles that have been faced so far. We investigated the stability of F impurities, and proposed a specific procedure to selectively introduce F on interstitial lattice sites.

The research was published in *Applied Physics Letters* [1]. It was one of the five most downloaded APLs in the month of November 2009 [2].

Results about fluorine were shared with the Mishra group. We also were given access to their experimental results on fluorine incorporation in devices and improvements in electrical characteristics. We performed many calculations of fluorine on nitride surfaces in an attempt to identify the underlying reason(s) for the beneficial effects observed in HEMTs, but no final conclusions have been reached to date.

3. Electronic structure of nitride surfaces

Many of the keys issues in nitride HEMTs revolve around the effects of the surface on the two-dimensional electron gas (2DEG), and hence on the transistor characteristics. As a first step, we performed a comprehensive study of the "bare" surface of the nitride semiconductor (i.e., without any oxide present). Such studies were in place for GaN, but still needed to be performed for AlN surfaces, in order to be able to draw conclusions for AlGaN layers. We studied both polar and nonpolar AlN surfaces, obtaining atomic reconstructions as well as the corresponding electronic structure. We found that the stable reconstructions generally satisfy the electron-counting rule, except for cases where Al adlayers are present. Trends among the group-III nitrides were identified.

For the dominant surface reconstructions, we analyzed the electronic structure with the goal of predicting Fermi-level pinning positions. One of the key conclusions was that the bare surfaces never have any surface donor state in the upper part of the band gap, showing that clean AlGaN surfaces cannot be the source of carriers in the two-dimensional electron gas in AlGaN/GaN HEMTs. This work has been published in *Physical Review B* [3].

4. Oxygen adsorption on GaN and AlN surfaces

Having established that bare surfaces cannot act as a source of electrons, we moved on to investigate oxidation of nitride surfaces. We first investigated the physics of oxygen adsorption. We found that under Al-rich conditions Al adatoms or O substitution on N sites can stabilize oxygen adsorption on the (0001) surface. We identified three stabilization mechanisms: (1) the electron counting rule; (2) oxide stoichiometry; and (3) changes in hybridization of the surface Al. In contrast to previous claims, we found that the O adsorption energies exhibit similar trends with increasing coverage for (0001) and (000-1) surfaces, showing that the energetics of O adsorption do not strongly depend on polarity.

This work has been accepted for publication in *EuroPhysics Letters* [4].

5. Oxidation of GaN and AlN surfaces

We then moved on to investigate realistic oxide layers on the nitride surface. Experimentally it had already been established that spontaneous oxidation is limited to one or two monolayers, a coverage regime that we explicitly addressed in our calculations. Numerous structures with different oxide coverage and different stoichiometry were examined, and their stability was interpreted in terms of driving mechanisms such as the electron counting rule and oxide-stoichiometry matching. Our results enable predicting which structures are likely to form under specific oxidation conditions. The calculated electronic structure then shows the expected position of surface donor states within the band gap [5].

We predict that the relevant structures have a distribution of occupied surface donor states in the band gap in a range between 1 eV and 3 eV below the conduction-band minimum (CBM). The highest occupied state is therefore considerably higher in energy than previously reported single surface donor levels, in agreement with recent experiments in the Mishra group [6] that show that the surface barrier height for low AlGaN thicknesses (i.e., at the onset of the 2DEG) can be as low as 1 eV. The integrated density of states of the relevant surface donor states is on the order of 10^{13} cm^{-3}, which means that the surface Fermi level moves down significantly as electrons are transferred out of the surface states into the 2DEG as the AlGaN thickness is increased. This finding explains the observed dependence of electron density on thickness and variations of surface barrier height [6]. We have also proposed explanations for the observed correlation between the surface barrier height at the onset of the 2DEG (which corresponds to the highest occupied surface donor state) and the magnitude of the density of surface donor states.

The studies on oxidized AlGaN surfaces were performed in collaboration with the Mishra group, as exemplified by joint publications [6,7].

6. Simulations of HEMTs

Having established that the relevant surface donors do not correspond to a single sharp level in the band gap, but to a *distribution* of surface states within the band gap, we proceeded to investigate how this finding would quantitatively affect the characteristics of the 2DEG. Previous simulations had been based on fairly simple models and had assumed only a single donor level

In contrast, we included surface donor states with distributed and finite density in Schrödinger-Poisson simulations of AlGaN/GaN layer structures [7].

These more sophisticated simulations not only agree with observed experimental trends [6], but in conjunction with our first-principles calculations allow us to propose specific microscopic mechanisms for the observed variations in surface barrier height and 2DEG density as a function of AlGaN thickness, Al composition of the barrier, and surface preparation conditions.

7. Nonpolar surfaces

As research on nitride-based HEMTs continues, increased attention has been focused on the use of nonpolar orientations. We have performed (as yet unpublished [8]) calculations of reconstructions and electronic structure of oxidized AlN and GaN non-polar (10-10) and (11-20) surfaces. Interestingly, the (10-10) surface favors a high-density oxidization structures formed by O substitutions for N along with O occupation of interstitial sites, whereas the (11-20) surface favors low-density oxidization structures formed by O_N and Al(Ga) vacancies on the surface. The high-density oxidization surfaces are more likely to form under O-rich conditions. In spite of the substantial changes in surface structure induced by oxidation, the positions of surface states in the band gap are not significantly affected and therefore there is little effect on the electronic properties of the materials. Given that in the case of nonpolar HEMTs the 2DEG is formed by intentional doping, these characteristics of the surface are likely to be beneficial.

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